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16. ABSTRACT

Four collection protocols for the heart-cutting procedure in ion chromatography were compared statistically to determine the best method for use in the analysis of trace ions in water. In the comparison, the protocols were applied in the analysis of 0.1 to 0.4-ppm AS(V) added to a municipal drinking water. Best precision was found when the collection was based on detector response rather than time and when collection included up to half of the next following major peak (SO_4^{2-}).

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Comparison of Collection Procedures for the Reinjection Ion Chromatography of Water

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Abstract

Four collection protocols for the heart-cutting procedure in ion chromatography were compared statistically to determine the best method for use in the analysis of trace anions in water. In the comparison, the protocols were applied in the analysis of 0.1- to 0.4-ppm As(V) added to a municipal drinking water. Best precision was found when the collection was based on detector response rather than time and when collection included up to half of the next following major peak (SO_4^{2-}).

Introduction

Efforts to improve resolution in column chromatography by subjecting a selected portion of a chromatogram to further chromatography have taken various forms. Deans (1) introduced valving to permit heart-cutting in gas chromatography (GC), shunting the desired portion to a second column. The more general terms "column switching" (2-4) or "multidimensional chromatography" (5) emphasize the gains to be made by changing mode or solid phase (2). On the other hand, "recycle," applied by Porath and Bennich (6) to gel chromatography, and Bombaugh and Levangie (7) to sorption liquid chromatography, refers to continuous return of the entire analyte to the same column, with removal of peak sides (8) or fully resolved peaks as they develop (7).

The authors have shown (9) that unresolved or hidden components in suppressed ion chromatography can be measured by heart-cutting, collecting the portion of the chromatogram (in suppressed eluent) on a concentrator column (10), and reinjecting on the same or equivalent column. This practice has been referred to as "recycle" (11) and "multidimensional" (9) but the authors tentatively prefer the term "reinjection" to denote that the chromatographic conditions remain the same—the improved resolution results entirely from the selectivity of the heart-cutting. Schomburg et al. (12) have used trapping in GC and the term "reinjection" has been applied (13) to trapping that collects, concentrates, and/or partially separates a sample prior to GC.

In previous work (9) it was found that the statistical precision with which trace components could be determined was much poorer than might be expected from the qualitative resolution of the peaks. This paper reports a statistical study of four protocols for defining the heart-cutting step. The authors chose to investigate additions of arsenate to drinking water because, at the previously determined conditions, arsenate elutes between the major components of nitrate and sulfate but does not require washing of the concentrator column to remove excess carbonate species (9). The criterion for optimization was least-squares minimization of deviations from a linear calibration based on four equally spaced concentrations: 0.1-, 0.2-, 0.3-, and 0.4-ppm As(V). The lowest concentration provided a distinct but unresolved peak in the original chromatogram.

Two pairs of cutting procedures were tested, one based on timing and the other on the response of the conductivity detector. Within each pair one cut was relatively narrow, rejecting nitrate and sulfate at the risk of losing some arsenate. The other was lengthened in the tail direction, including more sulfate.

Experimental

Apparatus

An ion chromatograph (Dionex, Model 2020i) was equipped with AS-3 separator columns for two systems. The suppressor for System 1, used for the initial sample injection, was an ASC-1 column. System 2 used a fiber suppressor continuously regenerated with 0.025*M* H_2SO_4 at a flow of 3.0 ml/min. The plumbing was modified to permit switching the effluent from the detector of System 1 either to waste or to a concentrator column which, in turn, could be connected to the injection valve of System 2. AG-3 concentrator columns were used both for the heart-cutting collection and also for the initial sample injection. The sample (exactly 10.0 ml) was loaded by an infusion pump (Harvard apparatus) and glass syringe with Teflon-tipped plunger (Hamilton). An eluent of 2.0m*M* $NaHCO_3$, and 1.5m*M* Na_2CO_3 at a pump rate of 2.0 ml/min was used in both systems. Both detectors were set at 10 μmho full-scale sensitivity

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and the outputs were recorded on a strip chart recorder (Hewlett-Packard) that operated at 0.1 in/min and could be switched between Systems 1 and 2 as needed. The detector of System 2 also was connected to a reporting integrator (Hewlett-Packard) that was enabled only for the reinjection portion of the run. The integrator was programmed for valley-to-valley baseline correction.

Materials

The sample matrix, city drinking water, was drawn from the tap and filtered through 0.2-μm pore size membrane (Metricel). The water contained no detectable arsenic. A stock solution of 1000-ppm As was prepared from reagent-grade $Na_2HAsO_4 \cdot 7H_2O$ in deionized water and was diluted to 10-ppm As in the matrix water. Final dilutions to the test concentrations were made immediately before each experimental block (see below).

Experimental design

The experiment was set up in blocks of runs that could be completed in half a day and that were limited to a single test concentration. Each block consisted of: regeneration of the System 1 suppressor, two trial injections from which parameters for the cutting operation were derived, and the four heart-cutting protocols, run in a pre-randomized order. Four consecutive blocks covered the four concentrations, also in a pre-randomized order. Six complete replications (24 blocks) were performed. Collection protocols were defined in the following manner. For each of the two trial runs of each block, the times were measured, to the nearest second, from injection, t_1 and t_2, of the valleys immediately before and after the arsenate peak, and the peak conductance, c, of arsenate. The values were averaged for the pair of runs and four collection procedures were followed in preassigned order: (A) Collection was started at the nearest half minute before t_1 and stopped at the next half minute after t_2. (B) Collection was started as in A and extended for exactly twice the time of A. (C) Collection was started when the conductance reached c coming down the preceding (NO_3^-) peak and stopped when the conductance reached c on the following (SO_4^{2-}) peak. (D) Collection was started as in C and continued until the sulfate conductance reached 10c or the peak maximum, whichever came first.

The protocols are illustrated in Figure 1, which shows the initial and reinjection ion chromatograms for 0.1-ppm As(V) added to drinking water. The shaded area on the left is the portion that was collected under Protocol C and the shaded area on the right is the measured arsenate peak after reinjection. The heart-cutting limits for Protocols A, B, and D are also indicated in the figure.

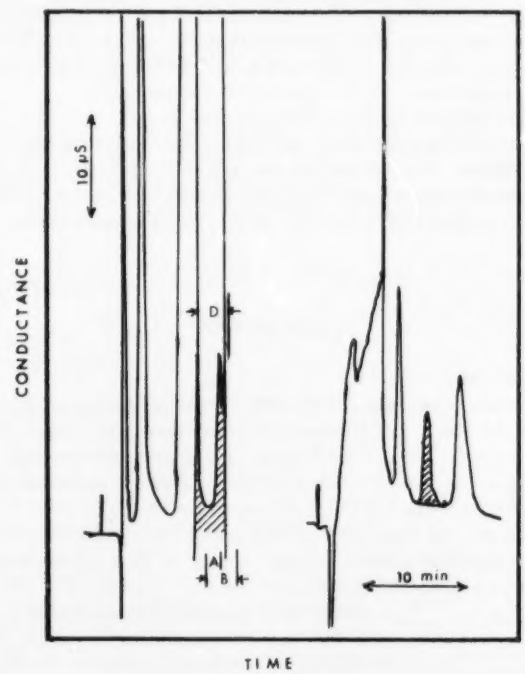

Figure 1. Reinjection ion chromatography of 0.1-ppm As(V) added to drinking water. Shaded areas represent collection Protocol C and the corresponding arsenate peak.

Results and Discussion

The data, consisting of arsenate peak heights and areas for 16 combinations of collection treatment and sample concentration, are summarized in Table I. In one block (Treatment B, concentration 0.4 ppm), the wrong collection protocol was inadvertently followed and the results were discarded. Two additional area measurements (Treatment B, concentrations 0.1 and 0.2) also were omitted. In one case, the integrator did not report a peak for arsenate because of poor resolution from sulfate, and in the other case, the reported area was anomalously low and accompanied by a diagnostic for baseline penetration. During the course of the experiment, as was observed in the previous work (9), the retention time of arsenate gradually shifted closer to that of sulfate, resulting in poorer separation in the later runs. No changes were made in the operating procedure.

The standard deviations of Table I show some tendency to

Table I. Peak Heights and Areas for Reinjected Arsenate

		Height (μmho)			Area (10^6 counts)		
Treatment	Concn. (ppm)	No. of replications	Mean	Std. dev.	No. of replications	Mean	Std. dev.
A	0.1	6	1.20	0.09	6	48	6
A	0.2	6	2.47	0.02	6	104	4
A	0.3	6	3.62	0.26	6	153	50
A	0.4	6	5.22	0.11	6	229	12
B	0.1	6	1.63	0.15	5	40	2
B	0.2	6	3.90	0.32	5	100	11
B	0.3	6	6.04	0.91	6	155	16
B	0.4	5	8.31	0.26	5	231	11
C	0.1	6	0.93	0.02	6	38	2
C	0.2	6	2.20	0.03	6	96	12
C	0.3	6	3 61	0.05	6	151	7
C	0.4	6	5.34	0.87	6	217	17
D	0.1	6	1.00	0.01	6	38	14
D	0.2	6	2.50	0.01	6	101	2
D	0.3	6	3.91	0.02	6	161	3
D	0.4	6	5.64	0.21	6	231	5

increase with concentration, but not proportionately. Table II presents least-squares linear calibration data by protocols. The parameters were not altered significantly by weighting points by the inverses of their variances. The calibration slopes are somewhat larger for the longer collection periods (Treatments B and D), reflecting more complete recovery of the arsenate. All the calibrations have negative intercepts, although not all are significant. This suggests a small systematic loss of arsenate independent of initial peak size. The variances of individual points and of the calibration curves both indicate that Treatment D is somewhat more reproducible than the others. Thus, the longer collection time is effective in recovering more of the trace component for reinjection, and inclusion of a substantial amount of the following peak does not interfere seriously in the subsequent resolution. The advantage of Treatment D over Treatment B indicates that basing the collection on detector response rather than time from injection removes some of the effects of varying retention time.

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Table II. Linear Calibration Parameters for Reinjected Arsenate

	Treatment							
	A		B		C		D	
	Est.	Std. dev.	Est.	Std. dev.	Est.	Std. dev.	Est.	Std. dev.
Peak Heights								
Intercept (μmho)	−0.17	0.21	−0.57	0.31	−0.64	0.24	−0.58	0.07
Slope (μhmo/ppm)	13.2	0.6	22.2	1.2	14.6	0.9	15.4	0.3
Std. dev. (y)	0.35		0.61		0.48		0.16	
Peak areas								
Intercept	−14	7	−25	6	−22	5	−27	4
Slope	591	26	626	22	591	18	642	14
Std. dev. (y)	14		11		10		8	

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